

Figure 6-57. IMPROVE/NESCAUM concentration for Shenandoah National Park: (a) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM Coarse; (b) chemical fraction of sulfate, soil, organic carbon (OC), and elemental carbon (EC); and (c) tracers.

60% of the fine mass during April through September and about 50% during the winter months. Organic carbon, on the other hand, range from 20% in summer to 30% in the winter months. The contribution of fine particle soil and elemental carbon is well below 5%. Throughout the year about 90% of the fine mass is accounted for by these measured substances. At the Shenandoah site, the sulfate aerosols constitute a higher percentage of the chemical mass balance, and lower percentages of organic carbon and elemental carbon than for the averaged nonurban Northeastern sites (Figure 6-29).

Chemical tracer data are shown in Figure 6-57c. The concentration of coal-tracer selenium shows two maximum, one during December through March, and another in June through September. Vanadium is relatively constant throughout the year. The fine particle sulfur concentration is almost a factor of five higher in August ( $3,300 \text{ ng/m}^3$ ) than in December ( $700 \text{ ng/m}^3$ ). This extreme sulfur seasonality is stronger at the Shenandoah site relative to the averages for sulfur seasonality at all nonurban Northeastern sites (Figure 6-29). The S/Se ratio has a remarkably smooth but highly seasonal variation that varies by about factor of four between the winter (700) and summer (2,600) values. If Se-bearing coal combustion is the exclusive source of sulfur at the Shenandoah National Park, then the sulfate production from the  $\text{SO}_2$  associated with coal-fired sources is 3 to 4 times higher in the summer than in the winter.

An examination of the nature and sources of haze in the Shenandoah Valley/Blue Ridge Mountains area (Ferman et al., 1981) showed that sulfate aerosols were the most important visibility reducing species. Averaging 55% of the fine particle mass, sulfates (and associated water) accounted for 78% of the total light extinction. The second most abundant fine particles, accounting for 29% of the fine mass, was organic carbon. The remaining particle mass and extinction were due to crustal materials.

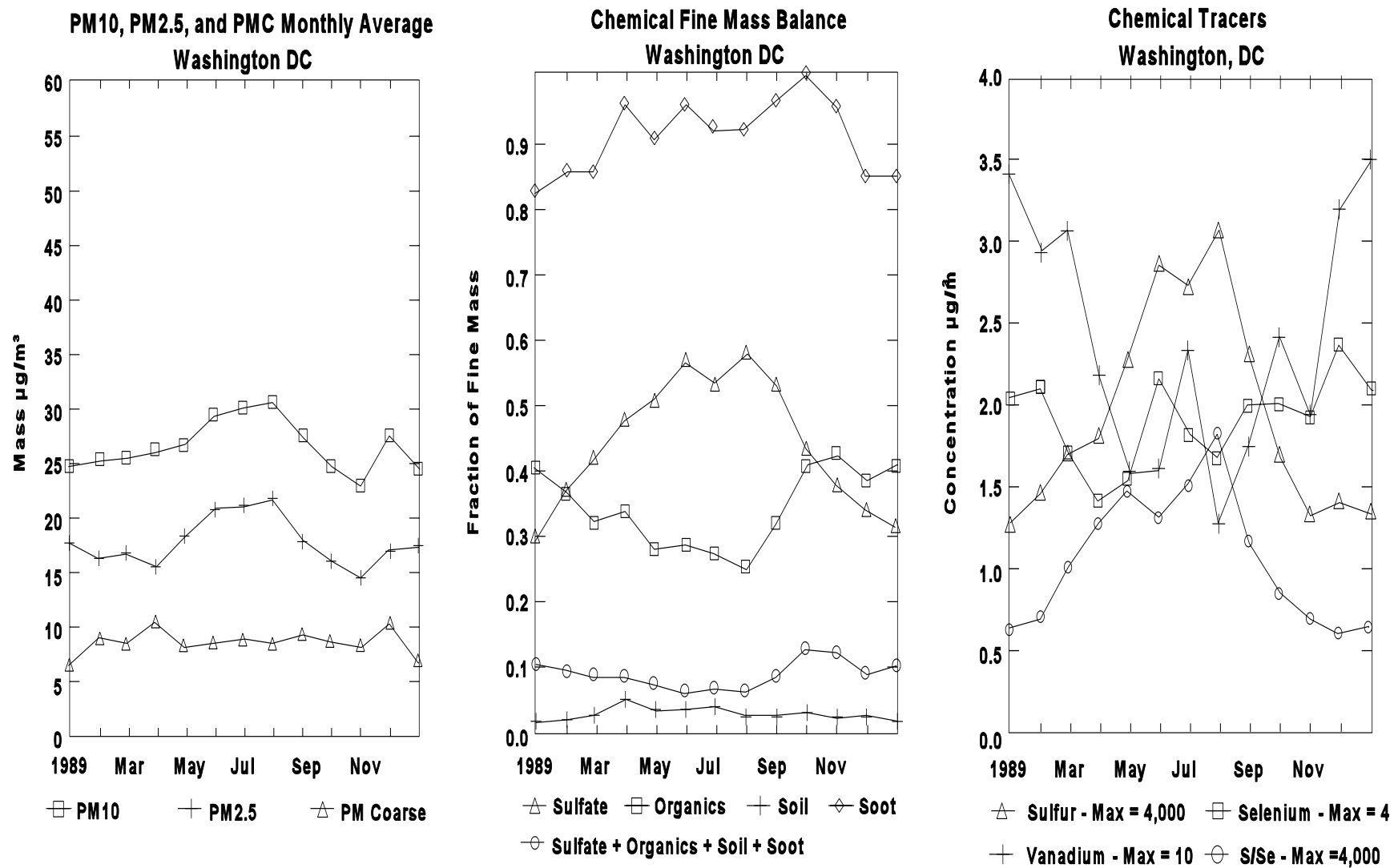
Using an in-situ rapid response measurement of  $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$  aerosol in Shenandoah National Park, VA, Weiss et al. (1982) found that the summer sulfate and ammonium ions average 58% of particle mass smaller than 1  $\mu\text{m}$ . The particle composition in terms of  $\text{NH}_4^+/\text{SO}_4^{2-}$  molar ratio ranged from 0.5 to 2.0 with strong diurnal variation. The particles were most acidic at 1500 EDT and least acidic in the period 0600 to 0900 EDT. The water contained in ambient aerosol particles was more strongly associated with sulfate and ammonium ions than with the remainder of the fine particle mass.

### 6.5.1.2 Washington, District of Columbia

The  $PM_{10}$  concentration at Washington DC (at the top of the National Park Service Headquarters building) is virtually constant over the seasons at 25 to 30  $\mu\text{g}/\text{m}^3$ . Fine particles contribute over 70% of  $PM_{10}$  throughout the year (Figure 6-58a). The weak seasonality in the fine particle mass is in sharp contrast to the factor of three seasonal fine mass modulation at the Shenandoah National Park. The coarse particle concentration in Washington, DC is 8 to 10  $\mu\text{g}/\text{m}^3$  throughout the year, exhibiting virtually no seasonality.

$PM_{2.5}$  at the urban Washington, DC site (figure 6-58b) is dominated by sulfates during the summer months (over 50%), but declines to 30% in January. Organic carbon, on the other hand, is 40% during October through January but only 30% during May through August. Thus, the relative roles of organics and sulfates at the Washington, DC urban site is fully phase shifted by half a year. Elemental carbon is a substantial contributor 9 to 12% during October through December. Fine particle soil contributes a low 2 to 5% to  $PM_{2.5}$  at this urban site.

The chemical tracer species are shown in Figure 6-58c. The concentration of the coal tracer selenium ranges between 1.5 to 2.0  $\text{pg}/\text{m}^3$  without appreciable seasonality. The urban Se in Washington, DC, is much higher than the Se at the northeastern nonurban sites. Vanadium, the tracer for fuel oil, varies by factor of two between the high winter values ( $>8 \text{ pg}/\text{m}^3$ ) and low summer values (3  $\text{pg}/\text{m}^3$ ). The pronounced V concentration seasonality is a clear indication of that the emissions from fuel oil and other vanadium sources are seasonal. The fine particle sulfur concentration varies by about factor of two between 1,400  $\text{ng}/\text{m}^3$  winter concentration, and about 3,000  $\text{ng}/\text{m}^3$  summer peak. The seasonal modulation of sulfur in Washington, DC is only factor of two compared to the factor of four fine sulfur modulation at Shenandoah National Park. The difference is primarily due to the elevated winter sulfur in Washington, DC. The S/Se ratio is about 600 in the winter and about 1500 in the summer. It differs from Shenandoah by the lower summer S/Se ratios. This result may be associated with differences in the air parcels involved in long-range transport and transformation of  $\text{SO}_2$  to sulfate at Shenandoah compared to Washington, DC.



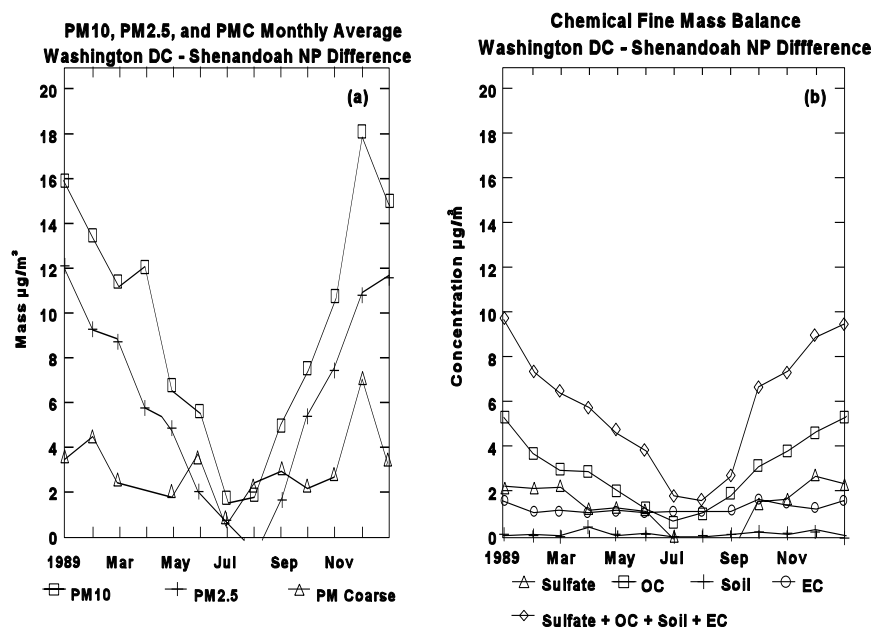
**Figure 6-58. IMPROVE/NESCAUM concentration for Washington, DC: (a) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>C</sub>; (b) chemical fraction of sulfate, soil, organic carbon (OC), and elemental carbon (EC); and (c) tracer concentrations.**

### 6.5.1.3 Comparison of Nonurban (Shenandoah) to Urban (Washington, District of Columbia) Aerosols

The Washington, DC, urban site and the companion nonurban Shenandoah monitoring site constitute a rare data pair that allows the quantification of urban-rural differences in fine and coarse particle concentration, and chemical composition. Within Washington, DC, industrial emissions are moderate compared to the industrial midwestern cities. However, both automobile emission density and emissions from winter time heating are expected to be high. In this section the excess aerosol concentrations in Washington, DC, over the Shenandoah site are examined to elucidate the urban influence.

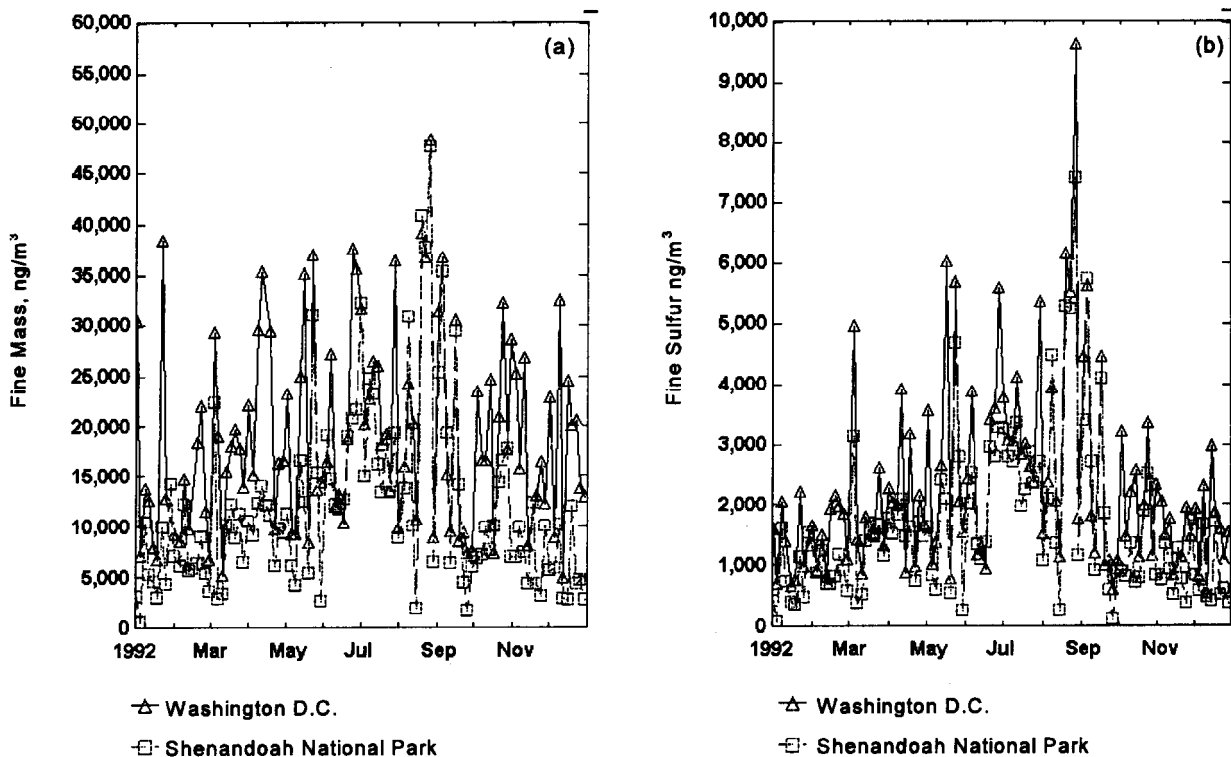
The Washington, DC, excess  $PM_{10}$  concentration (Figure 6-59a) ranges between 15-20  $\mu\text{g}/\text{m}^3$  in the winter, and  $<3 \mu\text{g}/\text{m}^3$  in the summer. Hence, there is almost an order of magnitude higher urban excess during the winter, compared to the summer. The seasonality of the excess  $PM_{10}$  is driven by the winter peak excess fine particle concentration of 10-12  $\mu\text{g}/\text{m}^3$ . The modest excess coarse particles is in the 3 to 6  $\mu\text{g}/\text{m}^3$  range throughout the year. Thus, the urban Washington, DC concentration exceeds its nonurban regional aerosol values during the winter season, and the excess winter time urban aerosol is largely contributed by fine particle mass. This indicates the smaller role of coarse particle fly ash, road dust resuspended by automobiles or construction, road salt and all other sources of urban coarse particles in Washington, DC, in winter.

The chemical composition of the excess fine particle concentration over the Shenandoah nonurban background is also shown in Figure 6-59b. Fine organic carbon dominates the urban excess ranging between 1  $\mu\text{g}/\text{m}^3$  during the summer, and 5.5  $\mu\text{g}/\text{m}^3$  during the winter. The seasonality of excess organic carbon also drives the seasonality of excess fine mass. There is an excess sulfate concentration of 1 to 2  $\mu\text{g}/\text{m}^3$  in Washington, DC, except during July, August, and September. In fact, in August in Washington, DC, sulfate concentration is about 0.3  $\mu\text{g}/\text{m}^3$  below the Shenandoah values. The urban excess elemental carbon concentration is 1 to 2  $\mu\text{g}/\text{m}^3$  throughout the year. The soil contribution to the fine particle mass is identical to the values of the Shenandoah National Park, yielding virtually no excess fine soil contribution in the urban area.



**Figure 6-59. Excess aerosol concentration at Washington, DC, compared to Shenandoah National Park: (a)  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , and  $\text{PM}_{\text{Coarse}}$  (PMC); (b) concentration of sulfate, soil, organic carbon (OC), and elemental carbon (EC).**

The short-term fine mass concentration at Washington, DC and Shenandoah National Park for the year 1992 is shown in Figure 6-60a. Although the sampling is conducted Wednesdays and Saturdays for 24 h, the data points have been connected. The figure also compares the daily (Wednesdays and Saturdays) fine particle sulfur concentrations at the two monitoring sites. The fine mass concentration time series for Washington, DC, show elevated concentrations ( $>30 \mu\text{g}/\text{m}^3$ ) that can occur throughout the year. On the other hand, high fine mass levels at Shenandoah are recorded only during the summer season. Particulate sulfur concentrations at the urban and nonurban site are often comparable during the summer (Figure 6-60b). This indicates that particulate sulfur often is a large part of the regional air mass that at any given day influences Washington, DC, and the Shenandoah National Park. Fine particle mass, on the other hand, shows an excess concentration at Washington, DC, particularly during the winter months. The fine mass daily time series clearly indicates that the concentration change from one daily sample to another can be an order of magnitude different. Consequently, most of the concentration variance is due to random synoptic air mass changes, and to a lesser degree due to periodic seasonal variations.



**Figure 6-60. Daily concentration of (a) fine mass and (b) fine sulfur at Washington, DC, and Shenandoah National Park.**

#### 6.5.1.4 New York City, New York

The New York City metropolitan area is characterized by high population density, moderate industrial activity, and relatively flat terrain. The  $PM_{10}$  concentration over the metropolitan area is shown in Figure 6-61a. The circles in the map show the locations of the monitoring sites and the magnitude of each circle is proportional to the average  $PM_{10}$  concentration at that site using all available data. The observed average concentrations change by about of factor of two to three from one location to another. Higher average concentrations tend to occur near the center of the metropolitan area.

In the New York City metropolitan area there was a decrease in the annual  $PM_{10}$  concentration between 1988 and 1994 from  $35 \mu\text{g}/\text{m}^3$  to  $27 \mu\text{g}/\text{m}^3$  for all sites and from  $41 \mu\text{g}/\text{m}^3$  to  $34 \mu\text{g}/\text{m}^3$  for trend sites (Figure 6-61b). The reductions were 23% for all sites and 17% for trend sites. There was unusually large difference between the two trends. The average

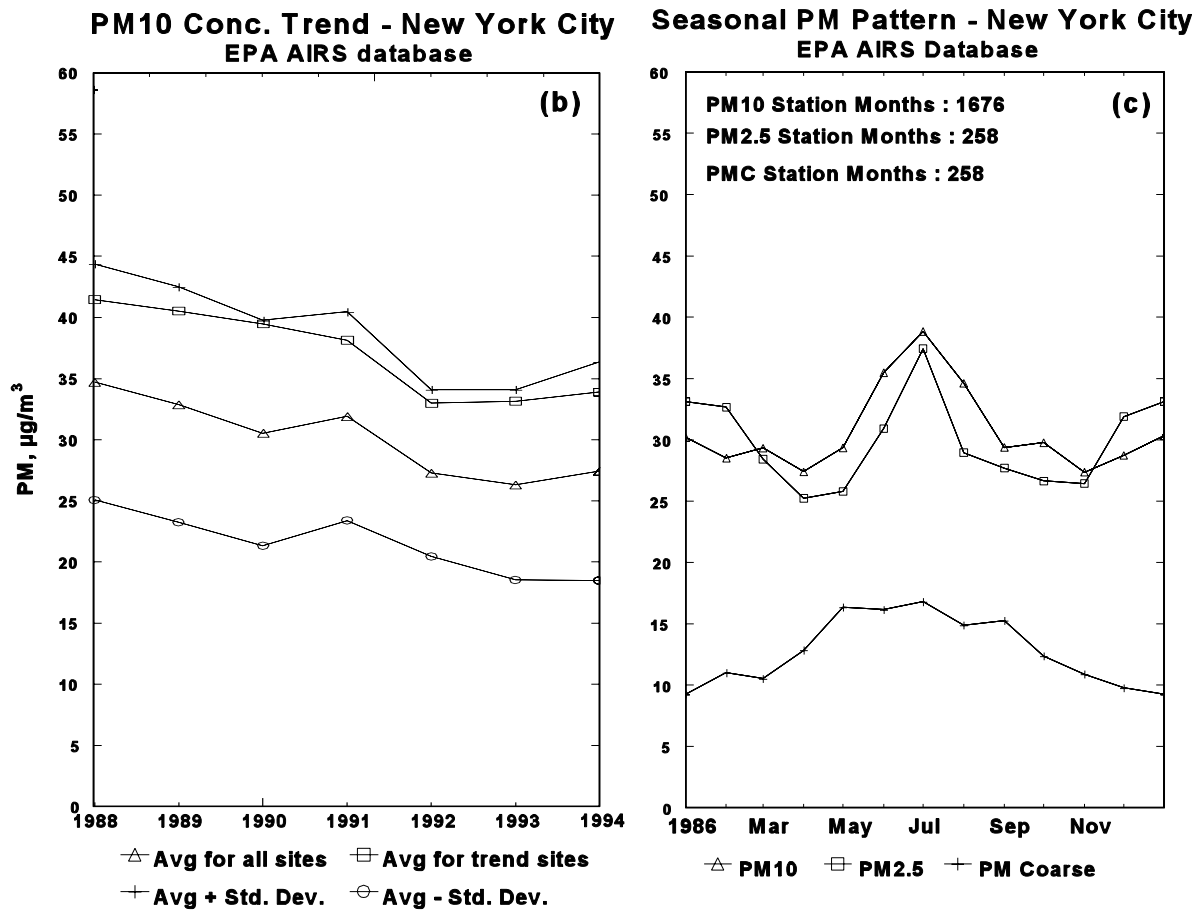
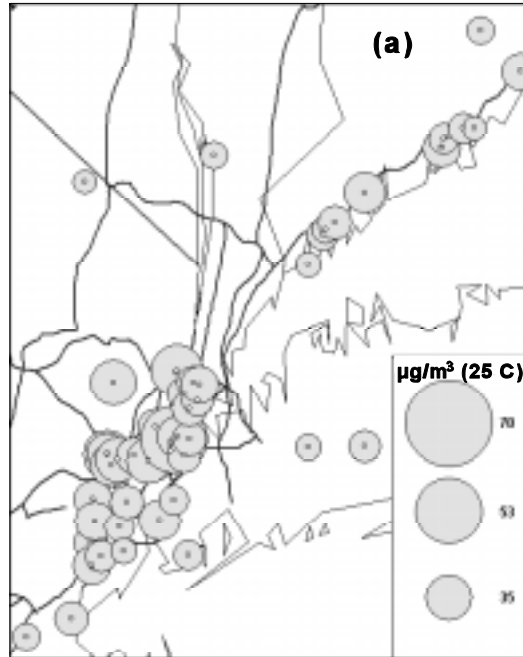


Figure 6-61. New York City region: (a) aerosol concentration map, (b) trend, and (c) seasonal pattern.



seasonal pattern over the subregion (Figure 6-61c) is 25 to 30  $\mu\text{g}/\text{m}^3$  throughout the year, but rises to about 40  $\mu\text{g}/\text{m}^3$  in July.

The seasonal pattern at three different individual monitoring sites in the New York City metropolitan area is shown in Figure 6-62a. The three sites all show similar seasonality with a summer peak, but with elevated concentrations closer to the city center.

Size segregated aerosol samples in New York City (Figure 6-62b,c) show that at both sites,  $\text{PM}_{10}$  concentrations are contributed primarily by fine particles. Based on the discussion of the more extensive Washington, DC (Section 6.5.1.2) measurements, it can be inferred that the summer peak in the fine mass is mainly due to the regional formation of the fine aerosols, while the winter peak is contributed by the local sources, confined to the inner metropolitan area.

As part of the New York Summer Aerosol study (Leaderer et al., 1978) continuous size monitoring confirmed the expected bimodal volume distribution with modes between 0.1 to 1.0  $\mu\text{m}$  and  $>3.0 \mu\text{m}$ . A number of interesting patterns were observed when the size distribution was averaged by hour of day. The diurnal average total number concentration showed a pattern which corresponded closely with the normalized diurnal traffic pattern. Particles  $<0.1 \mu\text{m}$  showed the most marked diurnal variation, following the total number curve. Moreover, particles in size ranges  $>0.1 \mu\text{m}$  showed little variation in the diurnal pattern. Analysis of samples processed by the diffusion battery indicated that approximately  $54\% \pm 18\%$  of the sulfate measured was in the suboptical range (approximately 0.04  $\mu\text{m}$  to 0.3  $\mu\text{m}$ ) with the remainder above 0.3  $\mu\text{m}$ . Little sulfate mass was found in particles in the nuclei range ( $<0.04 \mu\text{m}$ ). Analysis of impactor samples for sulfates consistently showed that more than 85% of all water soluble sulfates were  $<2.0 \mu\text{m}$  in size. Virtually no nitrate was present in the nuclei size range while the suboptical size range accounted for approximately 30% of the total nitrate. 70% of the total nitrate was found in the size range  $>0.3 \mu\text{m}$ . Analysis of large stages of Anderson impactor showed that approximately 50% of particulate nitrate was greater than 5.5  $\mu\text{m}$  in size.

Urban and rural particulate sulfur monitoring near New York City in the summer (Leaderer et al., 1982) indicated that sulfate concentration distributions were regionally homogeneous and increased with increasing ozone levels and covariant with several other pollutant and meteorological parameters. Sulfate concentrations correlated strongly with ammonium and strong acid at all sites. Strong acid concentrations were highest at the rural and semi-rural sites,

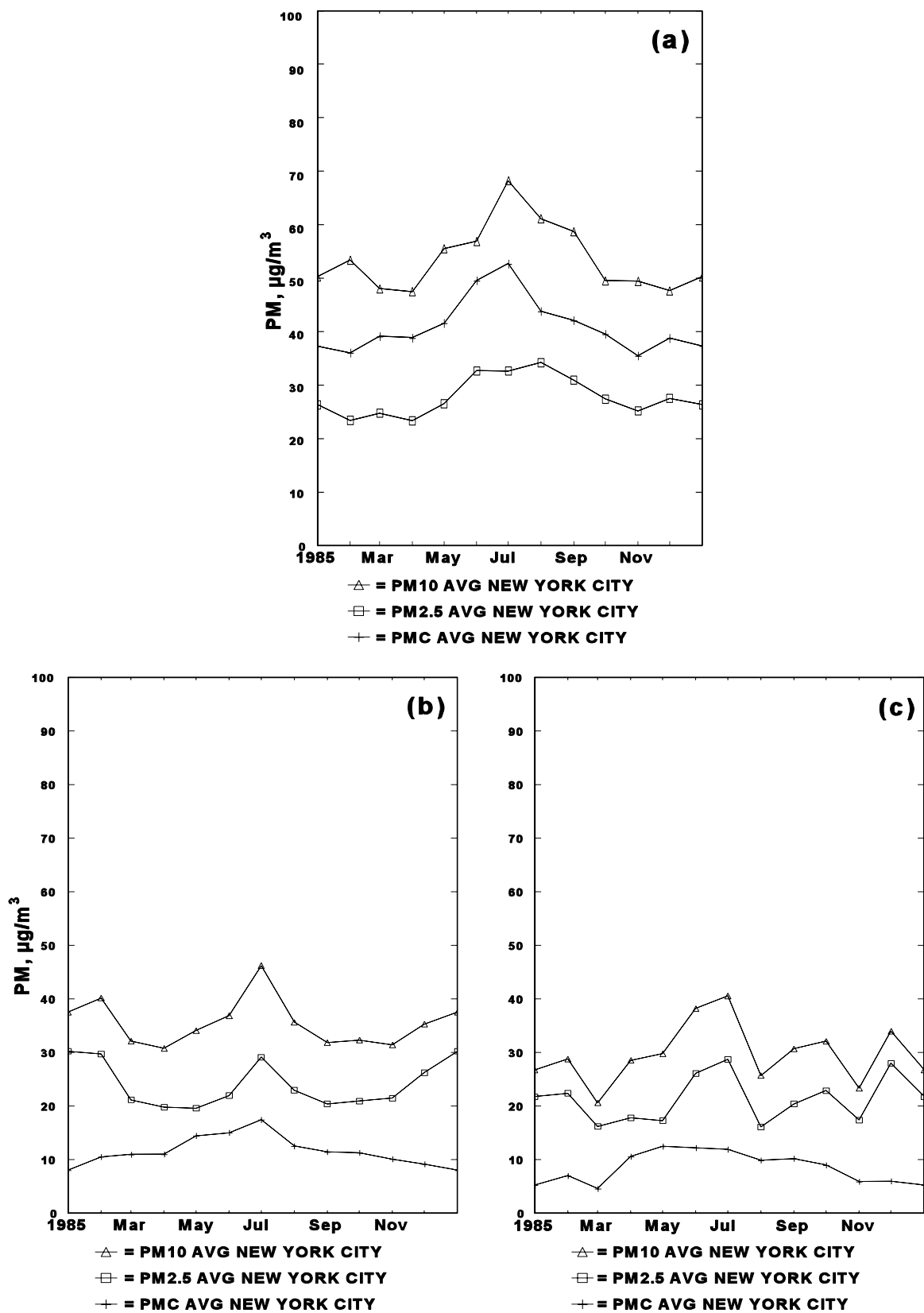


Figure 6-62a,b,c. Fine, coarse, and PM<sub>10</sub> particle concentrations at three New York City sites.

lowest at the urban sites, increased with increasing ozone levels and exhibited diurnal patterns which matched the ozone diurnal patterns.

Size dependent, mass and composition of New York aerosol for low, medium, and high visibility levels was reported by Patterson and Wagman (1977). At all levels of visibility, bimodal or multimodal particle size distribution were observed for total mass and for individual components. Decreased visibility corresponded to increased particle mass concentrations especially in the fine particle fraction. Increases in the proportion of particulate sulfate and to a lesser extent of nitrate, chloride, ammonium, and carbon were also associated with decreased visibility.

Aerosol pattern analysis of a major wintertime (1983) pollution episode near New York City in northern New Jersey (Lioy et al., 1985) revealed that the intensity of the episode was the greatest in the area of the highest commercial, residential and industrial activities, and that the atmospheric stagnation conditions resulted in the significant accumulation of aerosol mass. The aerosol mass was primarily fine aerosols, and the extractable organic matter comprising about 50% of the particle mass.

#### **6.5.1.5 Philadelphia, Pennsylvania**

The metropolitan area of Philadelphia includes urban-industrial emissions over flat terrain. Relatively uniform  $PM_{10}$  concentrations throughout the metropolitan area, with the exception of a single site (AIRS #421010149) in the middle of the urban area (Figures 6-63 and 6-64).

The downward trends in  $PM_{10}$  concentrations between 1988 and 1994 were largely or completely negated by the upward trends in 1993 and 1994 (Figure 6-63b). The decrease in annual  $PM_{10}$  concentrations at trend sites between 1988 and 1994 for all sites was from  $39 \mu\text{g}/\text{m}^3$  to  $32 \mu\text{g}/\text{m}^3$ , a decrease of 18%. The seasonal concentration of  $PM_{10}$  (Figure 6-63c) is about 30 to  $35 \mu\text{g}/\text{m}^3$  throughout the year, except during the summer months when it rises above  $40 \mu\text{g}/\text{m}^3$ .

The seasonal average  $PM_{10}$  concentrations for four sites near the center of Philadelphia is shown in Figure 6-64. The high concentration site noted on the metropolitan map in Figure 6-63a and two nearby sites in the industrial area long the riverfront are shown in Figure 6-64a. The average  $PM_{10}$  concentration at that site ranges between 100 to  $150 \mu\text{g}/\text{m}^3$

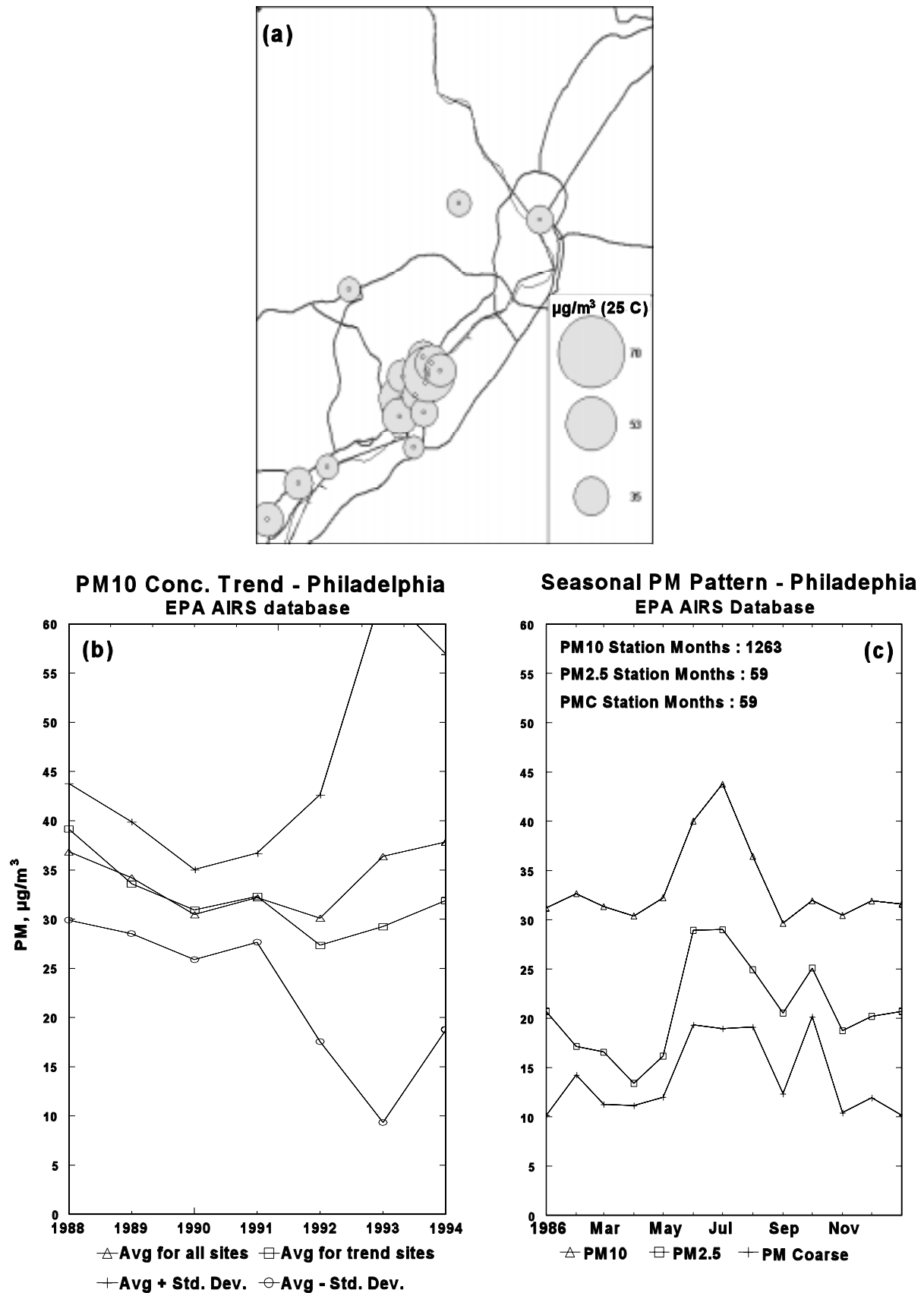
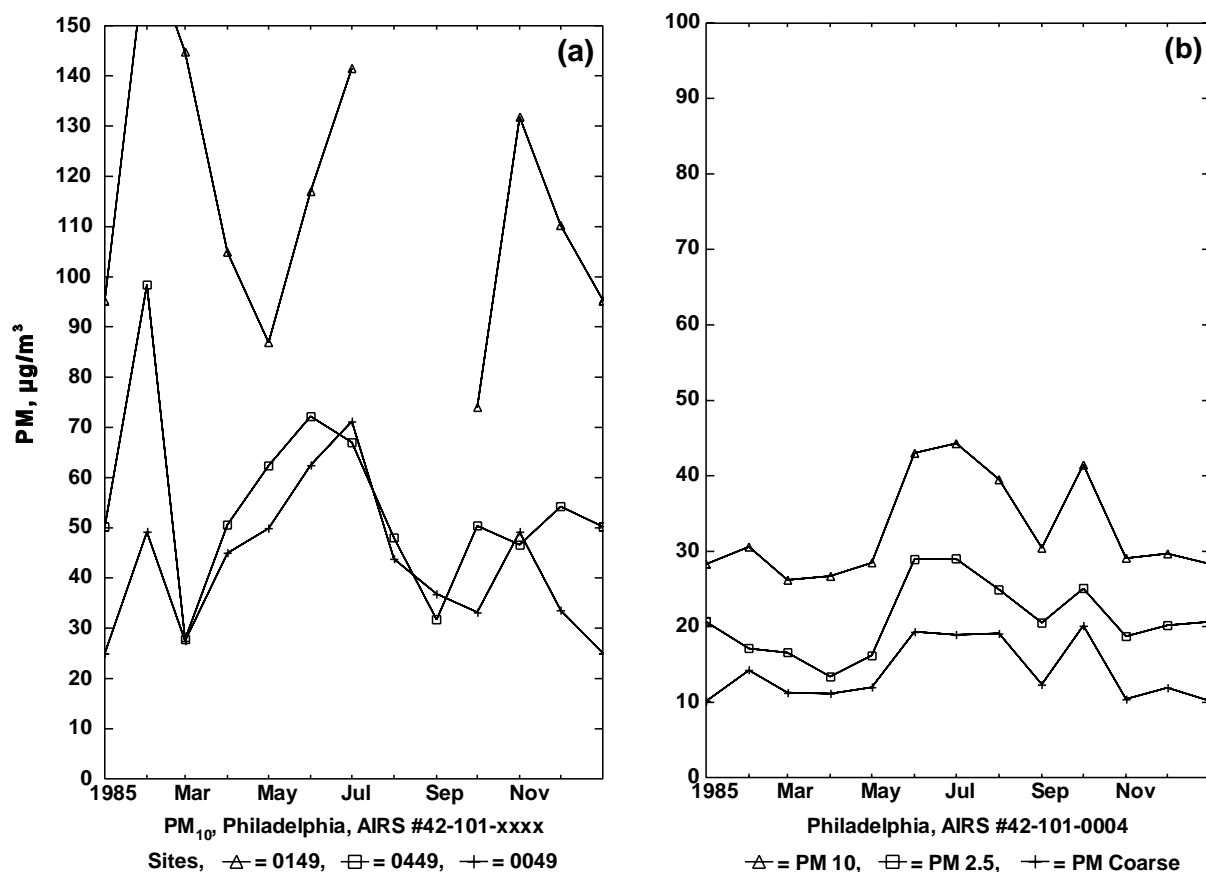


Figure 6-63. Philadelphia region: (a) aerosol concentration map, (b) trend, and (c) seasonal pattern.



**Figure 6-64a,b. Seasonal particle concentrations at four Philadelphia sites. (Note scale for (a) is  $150 \mu g/m^3$ .)**

which is a factor of 2 to 3 higher than the concentration at the neighboring sites. The daily concentrations at these source monitoring sites correlate poorly with a nearby site (Figure 6-64b) that is only 4 km away but outside the industrial area. This is an indication that the concentrations at the industrial sites are under the influence of a strong local source of  $PM_{10}$ . In contrast, community sites in downtown and suburban Philadelphia that are as much as 30 km apart show a strong correlation of daily measurements, indicating that a spatially uniform regional aerosol influences the daily values in Philadelphia.

Size segregated aerosol samples (Figure 6-64b) show that fine particles contribute more than coarse particles to the  $PM_{10}$  at this site. It is possible, however, that at other sampling sites, e.g., the industrial sites (Figure 6-64a), coarse particles may prevail.

Outdoor summertime sulfate ( $SO_4^{2-}$ ) concentrations were found to be uniform within metropolitan Philadelphia (Suh et al., 1995). However, aerosol strong acidity ( $H^+$ )